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Study on the Use of Ozonation Catalyzed by Nanoparticles for Ecological Cleaning Processes

Encarnación Jurado-Alameda*[a], José M. Vicaria[a], Otilia Herrera-Márquez[a], Vanessa Olivares[a], Génesis Sosa[b]

[a] Department of Chemical Engineering, University of Granada. Avda. Fuentenueva s/n, 18071. Granada (Spain)
[b] Universidad Simón Bolívar. 89000 Sartenejas, Caracas (Venezuela)
ejurado@ugr.es

The cleaning of dried gelatinized starch adhered to stainless steel fibers was studied in a cleaning device which simulates a CIP system. The influence of ozone, surfactant (fatty ethoxylated alcohol), temperature (25-45 ºC), pH (3-13), time (45 min), nanoparticles (Al2O3 and TiO2) and nanoparticle concentration (0.0-5.0 g/L) was analyzed. No detergency was obtained with pH from 3 to 9.6. At pH=13 and 45 ºC, the ozone increased the detergency value to 42%. The combined effect of ozone-surfactant produced high detergency (61.9 %) at high temperature (45 ºC), increasing the degradation of the wastewater generated. When ozone and Al2O3 or TiO2 aqueous suspensions were used jointly, the detergency did not increase but decreased. The nanoparticles were adsorbed to the starch.

1. Introduction

The cleaning process in the food industry is a critical operation. Specific protocols and chemical agents are required to achieve a clean surface, avoiding health problems and obstructions in production equipment (Liu et al., 2002). The effectiveness of the cleaning process depends on several factors such as the properties and fouling agent concentration, properties of the substrate, characteristics of the device, washing temperature, detergent formulation, hydrodynamic forces and time.

Ozone-based cleaning and sanitation operations present some advantages over those which involve common detergents and sanitizers, such as: (i) ozone decomposes rapidly and does not leave any toxic or undesirable residue; (ii) ozone can partially oxidize the organic matter and surfactant molecules present in the wastewaters from cleaning processes, reducing its chemical oxygen demand (COD) and thus facilitating its subsequent biological treatment (Guzel-Seydim et al., 2004).

There are several works that study the use of nanoparticles for the removal of pollutants from different substrates, analyzing the behavior in the solid-liquid and liquid-liquid interfaces (Chengara et al., 2004; Wasan and Nikolov, 2003). Different authors have published articles that studied the effect of nanoparticles on dirt starch (Peng et al., 2009) and their incorporation into detergent formulations used for cleaning starch, showing a positive effect on detergency (Soleimani et al., 2012, 2013). Wasan et al. (2010) also reported the use of nanofluids (aqueous suspensions of nanoparticles) in washing formulations. Furthermore, it has been found that catalysts Al_2O_3 and TiO_2 promote the TOC (total organic carbon) removal under the condition of neutral or alkaline buffer solution during catalytic ozonation of wastewater (Chou et al., 2009).

We have studied the cleaning of dried starch adhered to stainless-steel fibers using alkaline solutions, surfactants and ozone in the presence of Al_2O_3 and TiO_2 nanoparticles.

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2. Material and Methods

2.1 Materials

Cornstarch was used as soiling agent (Maizena,11.5% moisture, 0.29% fat, and 0.3% protein). A non-ionic surfactant called Findet 1214 N/23 was used (supplied by Kao Corporation S.A., Barcelona, Spain). It is a fatty ethoxylated alcohol with structural formula $R\text{-}CH_2\text{-}O\text{-}(CH_2\text{-}CH_2\text{-}O)_n\text{-}H$, carbon chain length C12 (70%), C14 (30%), average molecular formula (Bravo-Rodriguez et al., 2005),$C_{12.6}OE_{11}$, HLB=14.4, water content<0.3% in weight, critical micelle concentration=0.021 g/L (37 ºC) (Martínez-Gallegos, 2005).
The characteristics of the nanoparticles used, Al_2O_3 and TiO_2, are presented in Table 1.

Table 1: Characteristics of the nanoparticles.

Trade name	Composition	Specific surface area (m^2/g)	Size (nm)	Company
Aeroxide TiO_2 P 25	TiO_2	50 (approx.)	21 (approx.)	Evonik
Al_2O_3	Al_2O_3		13 (approx.)	Sigma -Aldrich

2.2. Substrate and soiling process

The solid substrate used was spherical wads of stainless steel fibers (Figure 1) (approx. 2 cm diameter, 0.80-0.85 g of weight). The soiling agent was a solution of gelatinized cornstarch (8% w/w). It was prepared heating the solution at 70 ºC for an hour (Souza and Andrade, 2002). When the solution is at room temperature the spherical stainless steel wads were soiled with the starch gel. The soiling process consists of the following stages: a) the surface of the wads was impregnated with the starch gel; b) the soiled spheres were dried for one day in an oven at 60 ºC; c) the dried soiled spheres were removed and weighed. By the weight difference, the mass of starch adhered on the steel surface was evaluated. The weight was similar. Eight spheres were used in every washing test, and the total mass was 2.0 ± 0.2 g.

Figure 1: Spherical wads of stainless-steel fibre with dried gelatinized starch.

2.3 Cleaning device operation

The cleaning assays were made in a modified Bath-Substrate-Flow system (BSF) proposed by Jurado et al., (2002) that includes an ozonation device (Figure 2). This experimental device simulates a cleaning-in-place system with ozonation. It contained a 1.5 L jacketed stirred tank (1) containing 1.2 L of solution, a peristaltic pump supplying 80 L/h flow (2), a glass column (50 mL of capacity, diameter 2.5 cm, height 8.5 cm) where the soiled substrate was located (3), a thermostatically controlled bath (4) and a gas diffuser (5). The O_3+O_2 flow diffused through a diffuser located at the bottom of reactor. The solution was extracted from the tank by the peristaltic pump, flowed upwards in the column, and finally returned to the tank. The flow recirculation maintained agitation in the solution. The temperature of the jacketed tank and packed column was kept constant using the thermostatic bath. The ozone generator (Anseros Peripherals COM-AD, Germany) used oxygen to produce the ozone on-site. The ozone concentration in the ozone-oxygen mixture was determined by an ozone analyzer (Ozomat GM-6000-PRO, Anseros, Germany). The ozone-oxygen mixture was introduced in the reactor (flow 40 NL/h, 42.3 g/m^3 ozone inlet concentration) by the diffuser. The gas leaving the system passed through gas washing flasks filled with a potassium iodide solution, in which the ozone oxidized iodide ions.

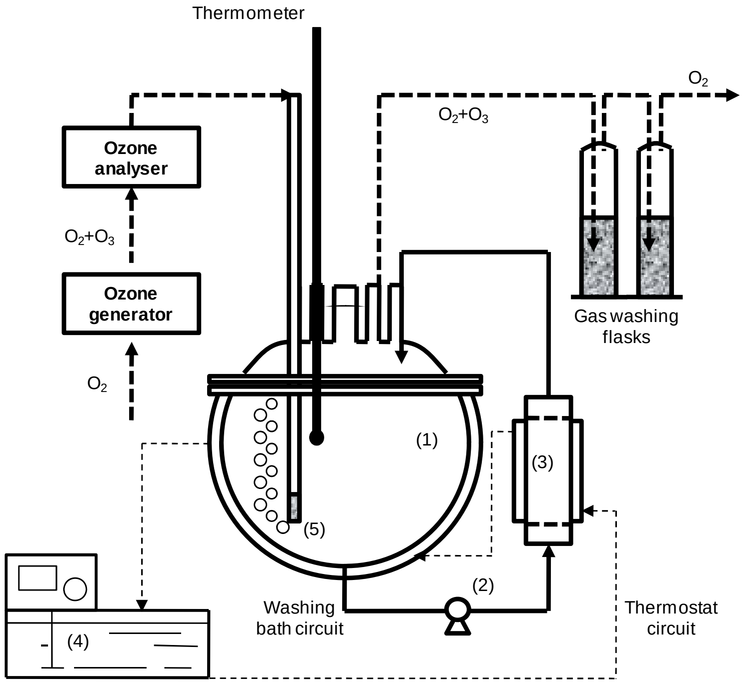

Figure 2: Scheme of the BSF with an ozonation device ("Washing bath circuit" is the circuit through which flows the washing solution; "Thermostat circuit" is the circuit through which flows the water used to heat the jacketed stirred tank).

2.4 Cleaning process

The cleaning procedure consisted: a) the washing solution is added to the jacketed stirred tank and the temperature was set; b) the soiled spheres were placed in the column; c) the pump was turned on, starting the cleaning process; d) after 45min of cleaning, the spheres were removed, e) finally, they were dried and weighted. The ozone concentration on the gas flow was 42.5 g O_3/m^3. In the experiments which the nanoparticles were included, they were dispersed in water by sonication for 30 min (Sonorex RK). Later the surfactant was added, and the solution was stirred for 5 min.

The detergency (De) or cleaning effectiveness was calculated from the dried starch removed from the substrate. The difference in weight between the dried starch adhered to the steel spheres at the beginning of the process ($m_{initial}$) and the dried starch adhered to the steel spheres after the cleaning process (m_{end}) allowed to calculate the detergency achieved as Eq(1):

$$De(\%) = \frac{m_{initial} - m_{end}}{m_{initial}} 100 \tag{1}$$

3. Results and Discussion

3.1 Cleaning process using ozone and surfactant

Starch is a widespread feedstock for industrial processes, especially in food manufacturing and processing, where it performs multiple functions such as water retention, bulking and gelling agent, thickener, and colloidal stabiliser (Singh et al., 2007). In industrial processes involving starches or their derivatives, these products often adhere to the surfaces and are difficult to eliminate, since starch residues show strong soil-substrate bonds to hard surfaces. Jurado et al.(2015) studied the detergency of dried starch adhered to steel surface using the same experimental device with a pH=13 buffer solution at 40ºC. After 45 min, the detergency obtained was 24 %. Detergency at lower pH was negligible

The cleaning effectiveness was evaluated using ozone. The variables assayed are shown in Table 2. At buffer pH=3, the use of ozone had little effect on the cleaning. The detergency values obtained were 3.4 % and 9.4 % for washing processes made at 25 and 45 °C, respectively. At buffer pH=9.6, the use of ozone had little effect on the cleaning too. The detergency values obtained were 2.6 % and 4.4 % for washing processes made at 25 and 45 °C, respectively.

At buffer pH=13, the use of ozone in the cleaning process allowed to obtain substantial improvements in the washing of dried starch adhered on steel surfaces. At 25 ºC the detergency obtained was 36.8 %, higher than that achieved in the absence of ozone (24 % by Jurado et al.(2015)). Similar results were obtained with ozone at 35 ºC. When cleaning was carried out at 45 °C, detergency increased to 42% (Figure 3). Therefore, higher detergency was observed at higher temperatures, although the concentration of ozone in aqueous solutions was lower when the temperature was higher as Henry's law indicated.

Table 2: Variables assayed in experiments with ozone and with/without 1 g/L surfactant.

pH	T (ºC)
3	25, 45
9.6	25, 45
13	25, 35, 45

Jurado et al.(2015) studied the detergency of dried starch adhered to steel surface using the same experimental device with a pH=13 buffer solution at 40ºC containing 1 g/L of Findet 1214 N/23. The detergency obtained was poor (21 %). At 25 ºC and buffer pH=13, no significant improvement was obtained in detergency when the washing solution contains ozone or 1 g/L of Findet 1214 N/23 and ozone.

In the present research, at pH=13, the detergency reached a value of 54.7 % at 35 °C when ozone and 1 g/L Findet 1214 N/23 are used jointly, increasing to 61.9 % when the assays were made at 45 °C (Figure 3). The combined effect of ozone-surfactant produces higher detergency: 61.9 % at 45 ºC with ozone-surfactant (Figure 3) vs. 21% at 40ºC with surfactant (Jurado et al., 2015) or 42 % at 45 ºC with ozone (Figure 3).

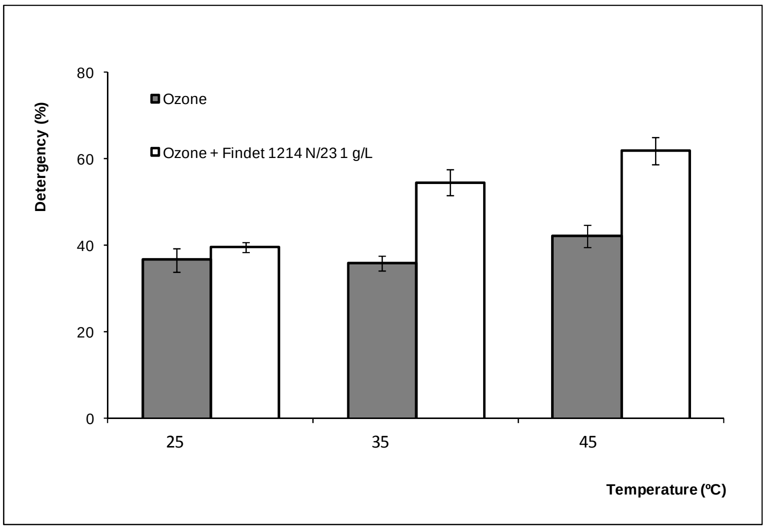

Figure 3: Detergency of dried starch adhered to the steel surface. Influence of the temperature. Surfactant (1 g/L), pH 13.0 buffer, time 45 m, flow ozone-oxygen (ozone concentration 42.3 g/m^3), recirculation flow 80 L/h. The error bars represent ± SD of 3–6 repetitions.

3.2 Cleaning process using ozone and nanoparticles

The effect that ozone and aqueous suspensions of nanoparticles, Al_2O_3 or TiO_2, produced on the cleaning of dried starch adhered to steel surfaces was studied at different temperatures and pH values. The variables assayed are shown in Table 3.

Table 3: Variables assayed in experiments with ozone and nanoparticles (without surfactant).

pH	T (ºC)	Al_2O_3 concentration (g/L)	TiO_2 concentration (g/L)
3	25	5.0	
	45	5.0	
9.6	25	5.0	
	45	1.0	
13	25	5.0	
	45	0.1, 0.5, 1.0, 5.0	0.1, 0.5, 1.0, 5.0

No detergency was obtained with aqueous suspensions, pH=3, that contains 5.0 g/L Al_2O_3 nanoparticles. Nor detergency was obtained when concentrations of 1.0 and 5.0 g/L of Al_2O_3 nanoparticles were tested at pH=9.6. At pH=13 and 25 ºC, the combined use of ozone and 5 g/L Al_2O_3 aqueous suspensions produced a value of detergency equal to -14.2 %. This means that the final weight of the soiled spheres was higher than the initial. It is due to the nanoparticles were adsorbed to the dried starch. Visually it was observed that the Al_2O_3 nanoparticles were adhered to the surface of starch and no elimination of starch was produced. At pH=13 and 45 ºC, different concentrations of Al_2O_3 and Ti_2O_2 nanoparticles were assayed, from 0.0 to 5.0 g/L. In all the experiments made with both nanoparticles at different concentrations, it was observed visually that the nanoparticles were adhered to the surface of starch.

The detergency values obtained with aqueous suspensions of 0.1 g/L nanoparticles was similar, 23.0 and 21.2 %, for Al_2O_3 and Ti_2O_2 suspensions, respectively (Figure 4). Qualitatively it observed that some cleaning occurred. When the nanoparticles concentration increases the behavior was different, depending of the composition. From 0.5 to 5.0 g/L the detergency diminished with both nanoparticles. This decrease in detergency was much greater withTiO_2 nanoparticles. So, the detergency observed with aqueous suspensions of 5.0 g/L Al_2O_3 was 1.6 %, whereas with 5 g/L of TiO_2 nanoparticles the detergency was -20.9 %. In both cases, visually no elimination of starch was observed.

The combined use of ozone and aqueous suspensions of Al_2O_3 or TiO_2 nanoparticles reduced the detergency of dried starch adhered on steel surface. This effect was greater with the TiO_2 nanoparticles, reaching values of detergency negative. This indicated that dried gelatinized starch adsorbed further TiO_2 nanoparticles.

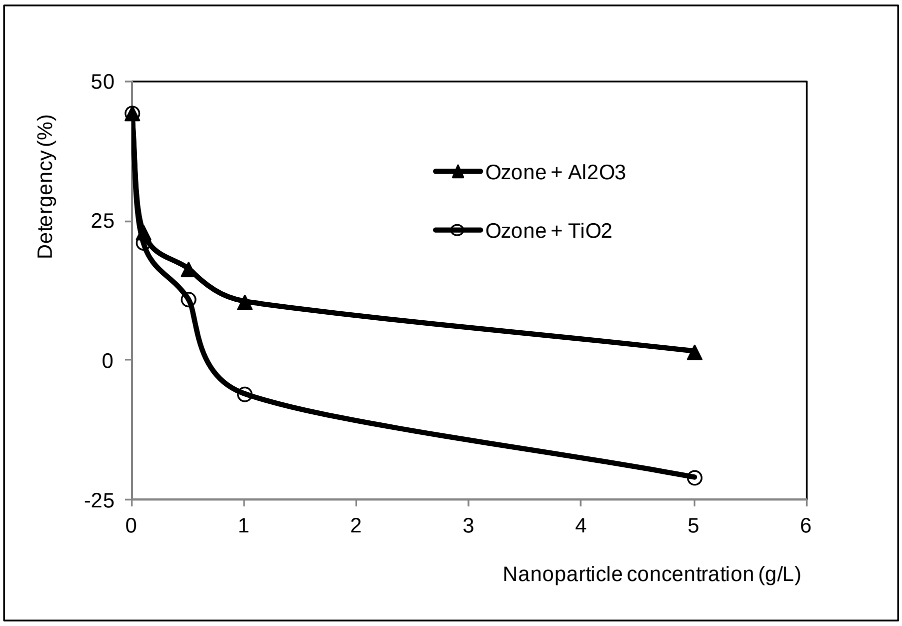

Figure 4: Detergency of dried starch adhered to the steel surface. Influence of nanoparticles. Buffer pH 13.0, 45 ºC, time 45 m, flow ozone-oxygen (ozone concentration 42.3 g/m^3), recirculation flow 80 L/h.

4. Conclusions

In the range analyzed, the dried gelatinized starch adhered to stainless steel was not cleaned using aqueous solutions containing ozone, fatty ethoxylated alcohol or Al_2O_3 or TiO_2 nanoparticles at pH values between 3 to 9.6 and temperatures between 25-45 ºC.

The use of ozone and pH=13 aqueous solutions to clean dried gelatinized starch adhered to steel surfaces was a suitable method. Higher detergency was observed at higher temperatures. The addition of Al_2O_3 or TiO_2 nanoparticles to the cleaning solution during ozonation did not increase detergency.

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